SCIENCE FOR GLASS PRODUCTION

SERVICEABILITY OF GLASS AND GLASSWARE (REVIEW)

Yu. A. Guloyan[1]

Research on the properties and characteristics of glass that determine the serviceability of the most massive glass objects and glassware is reviewed. The theoretical assumptions, general questions concerning the strength, chemical resistance (corrosion), and spectral characteristics of glass are noted. The properties and characteristics indicated are examined for sheet glass, glass fiber, and glassware.

The serviceability of glassware is characterized by a predominant indicator or group of indicators. For mass-produced articles (sheet glass, glass containers) high serviceability is achieved primarily by adequate strength, chemical stability, and the required spectral characteristic. All sheet glasses and glass containers must have adequate strength and chemical stability, while only certain types of articles require definite spectral characteristics (heat protective, heat reflecting, and other articles made of sheet glass; glass containers for medicines, wines, beer, juices, and certain other types of medical and food products; some types of glass containers must also have adequate heat resistance).

In the last few years the production of glass fibers has grown intensively as a result of the expansion of applications for articles based on them. Glass fibers are most widely used in composite materials where which strength is decisive. Despite high performance in other spheres of application (electric insulation, light guides, and so forth), strength remains a very important property of glass fibers.

Analysis of data obtained over a long period of time using the SkiGlass system [1] shows that investigations of operating properties and characteristics such as the CLTE, optical properties, and chemical stability, comprise a substantial fraction of all investigations performed. At the same time the number of investigations concerning strength, which is an important property, is clearly inadequate (about 1% over the period 1976 – 2001). Apparently, this is because the basic results of previous investigations and commercial developments are widely known. The existing methods for increasing substantially the strength of massive glass, specifi-

cally, sheet glass, are quite time-consuming and only of limited use. In this connection, large users of commercial glass, for example, in construction, prefer using low-strength but much cheaper glass and articles based on it.

The serviceability of glassware is directly related with the structure, state, and volume and surface properties of glass.

General questions concerning and the serviceability of sheet glass, glass fiber, and glass containers, which comprise about 90% of everything produced by the glass industry, will be examined below.

This review is based mainly on published review articles containing a substantial number of citations to original works

GENERAL STRUCTURAL CHARACTERISTICS OF GLASS

Inorganic glass, including silicate glass, exhibits characteristic structural features on different microscales [2 – 4].

In regions which have essentially atomic dimensions (region of short-range order), the mutual arrangement of the atoms and ions is relatively ordered and is reminiscent of the order in their arrangement in crystals. Branched chain structures formed predominantly by ionic-covalent bonds appear in somewhat larger regions. These structures form a three-dimensional framework permeating the entire volume of the glass, and they are indicative of the polymer structure of inorganic glass. In even larger micro-objects, regions with different chemical composition appear — this is a manifestation of nonuniform microscopic structure and microscopic separation. For extended microscopic nonuniformity, glasses can be viewed as microscopically separating systems with the colloidal-dispersed structures that are characteristic for many

[1] Scientific–Research Institute of Glass, Gus'-Khrustal'nyi, Vladimir Oblast, Russia.

solids, as is evidenced by experiments on leaching of glasses and the phenomenon of opalescence. All three types of structural features of glass can be intensified or weakened by changing the chemical composition or by heat treatment at high temperatures.

A characteristic feature of inorganic glass is the difference in the structure and chemical composition between the interior volume and the surface layer. This is due to the fact that under atmospheric conditions glass surfaces change immediately after the glass is formed, resulting in the formation of a thin surface layer whose chemical composition and physical-chemical properties differ from those of the rest of the glass. It has been determined that a silica film with very small thickness, fluctuating from 10 to 350 Å for different glasses, is formed on the surface of silicate glasses as a result of hydrolysis.

The structure of the surface layer can also change as result of diffusion of mobile ions from the bulk to the surface of glass, volatilization of some components during formation and heat treatment of glass, and ion exchange, the latter being used for special purposes to create stronger glass, glass with higher heat resistance, and so forth. The state of the surface layer also has a substantial effect on the chemical stability of glass [4, 5].

The spectral characteristics of silicate glasses are determined by the electronic structure of cationic-oxygen complexes of transition metals, distributed in the volume, with ionic coloration or colloidal nanoparticles of reduced metal ions (lead, copper, cobalt, and others) with surface electrochemical coloration of sheet glass. The factors determining the ionic coloration are analyzed in [6] from the standpoint of ligand field theory and the factors determining surface electrochemical coloring are analyzed in the review [7].

GENERAL QUESTIONS CONCERNING THE STRENGTH OF GLASS

Strength is the most important characteristic of glass and glassware, and for most massive articles it is the predominant property determining their serviceability. There are numerous investigations, which are generalized in [8 – 13], concerning the theoretical and practical aspects of strength.

Considering the modern requirements for buildings, structures, and technical facilities, construction and technical glass must be regarded not only as a safety material and as a light-transmitting material but also as a construction material which bears mechanical loads over an extended period of time [8, 14].

Theoretical and Technical Strength of Glass. *Theoretical strength* is a computed quantity for an ideal homogeneous defect-free material, subjected to quasistatic loads at sufficiently low temperatures. Theoretical strength largely depends on the nature and strength of the chemical bonds in the material. Relations between the theoretical strength and modulus of elasticity have been proposed for approximate calculations of theoretical strength. Given the modulus of elasticity it is possible to estimate the theoretical strength of glass ($\sigma \sim 0.1 - 0.4E$, where E is the modulus of elasticity), which lies in the range 7 – 20 GPa for different glass compositions [6].

Technical strength characterizes the strength of real articles. It depends on the surface state of the glass, the chemical composition of the glass, the degree of annealing, uniformity, composition, and temperature of the surrounding medium. The ultimate strength — the maximum stress under which the material fails under a static load — is a measure of strength. The ultimate strengths under tension, compression, bending, impact, torsion and so forth are distinguished depending on the form of the acting load. Glassware can withstand much higher stresses under compression than under tension and bending. The technical strength of massive glass articles (sheet glass) is 0.03 – 0.10 GPa under bending and tension and 0.5 – 1.0 GPa under compression. Commercial glass fibers are much stronger (1.8 – 3.5 GPa under tension). Even though the strength of commercial fibers is high, the variance in the data is still large. For example, for average strength 2 GPa the strength of individual samples of a commercial 10 μm in diameter lightguide lies in the range 0.5 – 3.5 GPa.

Comparing the theoretical strength with the real technical strength of articles made of massive glass (under tension and bending) shows that they differ by 2 – 3 orders of magnitude for different glass articles and glass compositions, though special treatment of glass has made it possible to reach strength values close to the lower theoretical limit [9]. In this respect, glass is not an exception; the technical strength of most existing materials is much lower than the theoretical value.

Structural and Surface Defects. In his monograph [10] G. M. Bartenev analyzes these defects. Structural defects are defects which arise spontaneously during the formation or heat treatment of glass. Structural defects in glass include imperfections of the real glass structure, i.e., microvoids in the glass-former network, structural imperfections due to impurity atoms, breaks in the framework formations, different kinds of superatomic and supermolecular formations, for example, micro-nonuniformities, and so forth. At the same time the elements of the micro-nonuniform structure (regions of micro-nonuniformity, their boundaries and joints) are not determining defects, since these are characteristic repeating structural motifs of real glass. From the standpoint of strength the real defect-free structure of glass is characterized by regular alternation of weak and strong microsections.

Real defects in the initial unstressed material are microscopic cracks which appear in weak locations as a result of thermal, mechanical, chemical, and other effects. In inorganic glass the weak locations are the interfaces between regions of microheterogeneity as well as locations which concentrate the residual microstresses which are always present in microheterogeneous glass.

The weakest locations and the most dangerous defects in glass, as a rule, are located on the surface. Consequently, the surface strength of glass is usually less than the bulk strength. Submicrocracks and microcracks of different nature and origin are surface defects. As a rule, these defects are so small that they cannot be seen with the unaided eye or under an optical microscope, so that special methods are used to reveal such defects [2]. Surface microcracks appear in glass as a result of local concentrations of stresses arising for various reasons, specifically, because of local mechanical damage and sharp temperature differences.

Brittle solids (glass) can be conventionally divided into low- and high-strength according to the mechanism and character of the failure.

Low-strength glass initially contains surface microcracks and other defects with different degrees of danger. Under load microcracks in such glass are the foci of failure. The mechanism of failure of low-strength glass, also called athermal failure, can be explained by Griffith's theory. This mechanism is realized at sufficiently low temperatures or high rates of failure, when crack growth is determined mainly by the elastic properties of the solid and the elastic energy stored in it and not by thermal fluctuations.

High-strength tempered glass subjected to chemical etching and high-strength defect-free glass fiber contain virtually no surface microcracks. The phonon concept within the framework of the thermal fluctuation theory can be used to explain the mechanism by which high-strength glass fractures. Since there are no surface defects in high strength glass, the most likely locations where bonds rupture are sections of the micro-nonuniform structure of the glass. The fracture of high-strength glass into many fragments reduces mainly to the development of many identical nuclear defects simultaneously in the entire volume of the sample which under stresses and thermal motion become microcracks.

Statistical Theory and Evaluation of the Strength of Glassware. The main assumptions of the general statistical theory of strength can be reduced in the following:

defects of different origin and presenting different degrees of danger our present in samples of the same material, and outwardly identical samples obtained by the same technological method can have defects presenting different degrees of danger;

the most dangerous defect determines the strength of a sample in a uniformly stressed state;

the larger the volume (or surface) of a sample (glassware), the more likely that the most dangerous defects will be present.

On the basis of these assumptions and taking account of the micro-nonuniform structure, the strength of glass and glassware is usually evaluated using distribution functions which show not only the value of the strength but also the variance appearing in the data as a result of the character of the defects.

The heat resistance of glass and glassware is directly related with their mechanical strength. Heat resistance also
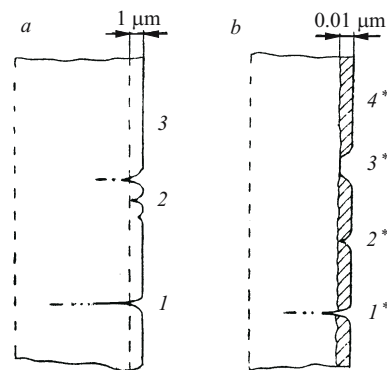

Fig. 1. A schematic diagram of surface defects in bulk (sheet) glass (*a*) and glass fiber (*b*). *In the transverse section of sheet glass*: *1*) microcracks extending to depth 0.1 – 1.0 mm into the glass; *2*) microcracks several microns deep; *3*) glass surface after the removal of a surface layer by chemical etching; *in the transverse section of a glass fiber: 1**) microcracks 0.1 – 1.0 µm deep; *2**) submicrocracks less than 100 Å deep; *3**) microruptures of a structural surface layer; *4**) undamaged surface of a glass fiber.

depends on the strength of the thermal action, the chemical composition, the thickness of the glass, the dimensions and the shape of the glassware, and other factors. The heat effect can be local or global (over the entire surface of the glassware).

When glass is exposed thermal action, tensile stresses arise on cooled surfaces and compressive stresses arise on heated surfaces. Since the strength of glass under compression is much greater than under tension, the heat resistance of the glass during cooling is lower than during heating.

The heat resistance under otherwise the same conditions depends, first and foremost, on the CLTE and the mechanical strength of the glass. Consequently, glass with high heat resistance is obtained by using special compositions (to decrease the CLTE) or by increasing the mechanical strength of non-heat-resistant glass (annealing, ion exchange) [8, 11].

STRENGTH OF SHEET GLASS AND GLASS FIBER

Levels of Strength. The classification of glass, mentioned above, as low- and high-strength is not absolute by any means. In this connection, G. M. Bartenev proposed on the basis of an analysis of a great deal of experimental data a more accurate classification of the levels of strength of glass [10]. According to this classification, the levels of strength are more or less distinct values of strength around which samples or articles containing defects cluster (Fig. 1).

Approximate values of the strength levels for commercial sheet glass and glass fiber in the aluminosilicate group in tests performed under atmospheric conditions and in vacuum at 20°C (the loading time is approximately 10 sec) are presented in Table 1 [10].

Strength distribution for sheet glass. There are many works devoted to investigations of the strength of sheet glass.
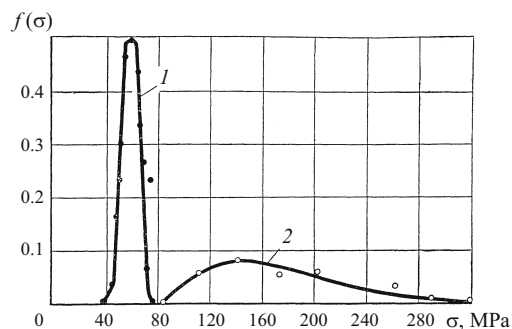
Fig. 2. Strength distribution of 2.3 mm thick samples of sheet glass: *1*) under transverse bending (the damaged edges are under a load); *2*) under symmetric bending (the edges lie outside the loading zone).

These works are systematized in the monographs [8 – 12]. Figure 2 displays the typical strength distribution curves for samples of sheet glass which differ by the state of the edges and surface [10]. The curve 1 characterizes the strength distribution function of glass samples with damaged edges (cutting, grinding). The values of the glass strength are minimal, and the variance of the test results is small. The most dangerous edge defects arise during cutting with diamond and also during grinding. The small variance in the values shows that the edges of the samples have defects of approximately the same degree of danger. The curve *2* shows the variation of the surface strength of samples of sheet glass. The average value of the strength has its maximum in this case. The large variance of the values shows that the surface of the glass contains a large collection of defects with different degrees of danger.

The analogous curves presented in [8 – 12] are associated with a different surface state and the use of different methods of hardening. The average data on the strength of sheet glass hardened by different methods are presented below.

Hardening method	Ultimate bending strength, GPa
Initial glass (no working)	0.03 – 0.10
Annealing in air	0.12 – 0.20
Annealing in liquid, devitrification	0.20 – 0.40
Ion exchange.	0.30 – 0.70
Etching.	1.00 – 1.70
Combined methods (ion exchange + annealing in air, etching + adhesion protective layer, etching + ion exchange). . . .	1.70 – 2.50*

* The ultimate strength of glass can reach 5 GPa when etching is used [9].

Research on the construction strength and longevity of glass articles based on sheet glass has been picking up in recent years [15 – 17].

Strength distribution for glass fiber. The modern formation technology makes it possible to obtain glass fiber that is much stronger than bulk glass, specifically, sheet glass.

According to the data in Table 1, for aluminoborosilicate glass fiber there are three distinct levels of strength: 0.6 – 1.3, 2.0 – 2.5, and 3.0 – 3.5 GPa. The high strength of glass fiber is explained by the conditions under which the surface layer and the volume part of fiber are formed during the production process.

As the fiber is drawn, a surface layer forms in the presence of an elevated gradient of temperatures and viscosities at the surface and inside an "onion." Considering the small diameters of the fiber being drawn, the very thin surface layers cooled rapidly and strengthening compression stresses appear in it. As a result, a substantial radial thermal gradient

TABLE 1.

Strength level	Surrounding medium	Approximate strength level, GPa		Type of defects*
		bulk glass	glass fiber	
1*) corresponds to low-strength bulk glass after mechanical working	Atmosphere	0.03 – 0.06	Not realized	Macrocracks arising during mechanical working
2*) corresponds to low-strength sheet glass after formation and glass fiber after heat treatment or prolonged storage	Atmosphere	0.05 – 0.10	0.1 – 0.2	Surface microcracks appearing during the formation of bulk glass or during heat treatment of glass fiber
	Vacuum	0.10 – 0.40	0.2 – 0.4	
1) corresponds to high-strength sheet glass, including glass protected from damage, or low-strength glass fiber	Atmosphere	0.15 – 1.00	0.6 – 1.3	Surface of microcracks formed during the formation of thin sheets of glass and glass fiber on 50 – 100 Å micro-nonuniformities
	Vacuum	–	1.2 – 2.6	
2) ultimate strength of the structure real micro-nonuniform bulk glass and glass fiber after removal of a surface layer	Atmosphere	2.00 – 2.50	2.0 – 2.5	"Defect free" bulk glass (after etching) and micro-fractures arising in the surface layer of a glass fiber during the formation of the fiber
	Vacuum	3.50 – 4.50	3.5 – 4.5	
3) ultimate strength of glass fiber (with an undamaged surface later)	Atmosphere	Not realized	3.0 – 3.5	Defect-free glass fibers
	Vacuum	Same	4.0 – 5.0	
4) expected theoretical strength	"	7 – 20	7 – 20	Ideally homogeneous glass structure

* The characteristic defect sizes are presented in Fig. 1.

of stress arises and during drawing the glass layers move with different velocities. The maximum velocity and stress are concentrated in a thin surface layer.

It follows from all experimental data taken together that the high strength of a glass fiber is explained by the relatively high strength of the very structure of real glass, by the existence of a strengthened surface layer, as well as by the technological features of the glass-fiber production, eliminating the appearance of dangerous surface defects which damage the structural surface layer. The strength level of fibers with surface defects can be increased by etching away the defect and surface layer.

The improved production technology makes it possible to obtain virtually defect-free fibers, having a third level of strength (see Table 1). Etching of defect-free glass fibers decreases their strength, since the process removes the strengthened surface layer. Disruptions of the technology, treatment, and prolonged storage of glass fiber decrease its strength as result of the appearance of more dangerous surface defects.

The dependence of the strength on the conditions under which fibers are obtained is generalized in [10, 13]. Analysis of the curves of the strength distribution of glass fibers in different states shows that the increase of fiber strength from low- to high-strength fibers is accompanied by a decrease of the variance of the strength values and an increase of the probability for reaching the corresponding strength values.

GENERAL QUESTIONS CONCERNING THE CHEMICAL STABILITY AND CORROSION OF GLASS

It is shown in the works of I. V. Grebenshchikov and other investigators that as a result of the effect of water on a freshly prepared glass surface, hydrolysis with hydrated silicates and hydroxides being formed occurs.
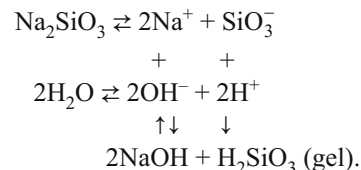
The interaction scheme can be represented as follows:

$$[\equiv Si - O -] - Si - ONa + H_2O \rightarrow$$
$$[\equiv Si - O -] - OH + NaOH.$$
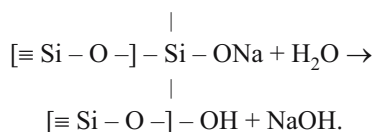
Soluble alkali-metal hydroxides, dissolving in water, easily leave their formation site. Low-solubility hydroxides remain on the glass surface together with a silica framework, whose composition corresponds to that of condensed silicic acids. The surface layer that appears differs from the initial glass by a high concentration of silicon oxide, and the layer is permeated with ultrafine pores filled with the products of hydrolysis. The alkali-metal hydroxides and salts which have formed, dissolved in water, and remain on the surface destroy the surface silica layer via the reaction

$$[\equiv Si - O - Si] - O - Si \equiv + NaOH \rightarrow$$
$$[\equiv Si - O - Si \equiv] - OH + Na_2SiO_3.$$
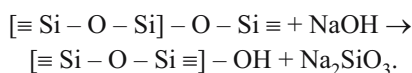
The following reaction occurs as a result of hydrolysis:

$$Na_2SiO_3 \rightleftarrows 2Na^+ + SiO_3^-$$
$$+ \qquad +$$
$$2H_2O \rightleftarrows 2OH^- + 2H^+$$
$$\uparrow\downarrow \qquad \downarrow$$
$$2NaOH + H_2SiO_3 \text{ (gel)}.$$

The silicic acid gel which forms on the surface and has an open structure permeated with pores facilitates the diffusion of water and NaOH to glass sections located under the gel layer, thereby intensifying the destruction of the glass. Thus, the appearance of silicic acid gel is an indication that the glass is undergoing corrosion. At the same time the formation of such a gel is a quite prolonged process because of the low concentration of H^+ ions in the alkaline solution that arises under the reactions indicated above, where the glass interacts with water and condensed alkali compounds, which formed as alkali oxides partially evaporated during glass formation, dissolve.

The factors associated with the chemical stability of silicate glasses are examined in detail in the reviews [5, 18].

SERVICEABILITY OF GLASS CONTAINERS

The main serviceability factors for glass containers are:

strength of the glass articles (mechanical and thermal);

chemical stability of the glass (resistance to chemical corrosion);

spectral characteristics of glass: photoprotective power for some types of food products and medicines, no appreciable color tones for colorless containers.

These are the determining factors for evaluating the general quality of glass containers. These factors will be examined mainly in application to bottles used for beverages, since such bottles represent the bulk of the glass container-ware produced.

The **strength** of a glass container determines how well food products are preserved: the higher the strength, the smaller the losses of food products during packaging, storage, and consumption are.

The following have the greatest effect on the strength of a glass container:

degree of uniformity of the glass mass;

formation and annealing regimes of glass articles;

character of the packaging, shipment, and usage of the articles;

methods for increasing and preserving the strength of articles.

Degree of glass mass uniformity. The quality of the initial materials, the way charge and cullet are loaded into the furnace, the temperature regime of the glassmaking furnace, and the use of means for intensifying glassmaking all have a large effect on the degree of uniformity of the glass mass. The following possible rough disruptions of glass mass uni-

formity should be noted: solid (stones), glassy (cords), and gaseous (bubbles) conclusions. Silent inclusions are especially dangerous; they create the danger of stress concentration that cannot be removed by annealing, and this can result in fracture of the articles. In the absence of foreign inclusions, the uniformity of chemical composition in the interior volume of the glass mass, the degree of which is determined by the level of the glassmaking technology, plays an important role.

Variations of the composition of the initial materials (especially quartz sand), which are due to fluctuations of the content of the main and coloring oxides, as well as an unstable temperature regime of glassmaking have a negative effect on the uniformity of the glass mass.

Glassware formation and annealing regime. The process used to make a glass container determines the strength of the container. This is the most complicated and, at the same time, least controllable process in the entire technological cycle.

Various types of defects, which can be determined visually or using automatic monitoring equipment and which lead to rejection of articles, are the most obvious manifestation of a disruption of the formation regime. However, articles with no obvious defects often do not pass tests for strength or fracture in the modern, high-speed packaging lines. This is due to hidden defects, which fall within the limits of admissible or undetermined (during monitoring) defects and manifest only under high mechanical and variable thermal loads. Examples of hidden defects are micro-openings and nonuniform glass distribution over the thickness (volume) of an article.

Important factors affecting the quality of articles are the optimal shape of the articles, the correspondence to the shape to that of a drop, the preliminary and finishing molds, and the quality and temperature of the working surface of the molds.

During annealing, the internal residual stresses which are formed during molding are removed or decreased to admissible limits. This is an important stage in preserving the strength of articles, so that adherence to the technological annealing regime is paramount. The construction of modern annealing furnaces creates the conditions for fully adequate and high-quality annealing. In addition, to improve heat transfer articles should not be arranged too close to one another. Articles must not be allowed to fall. The presence of IR components which improve the conditions for heat transfer increases the quality of annealing.

Character of packaging. The quality of a glass container reaching users depends largely on the method used to package the container. Packaging protects a container from mechanical effects during shipment, which could damage the container during loading and unloading operations and transport. Packaging also protects containers from contaminations. Foreign practice and the experience of domestic works show that the best method for packaging glass containers is container-free packing using heat-shrunk polyethylene wrap. Large packages are formed on pallets; small packages are made without pallets.

Increasing the strength of glass containers. The most readily available, cost-effective, and widely used method for increasing the strength of glass containers is depositing a protective-strengthening coating on them [19]. Inorganic and organic coatings are used; these coatings substantially change the properties of the glass surface and improve the mechanical characteristics of the articles, specifically, such coatings increase the water repellency of the surface, which in turn decreases the weakening effect of surface-active media, first and foremost, moisture in the air. At the same time, the surface of glassware is protected from abrasive action by different bodies and particles, which increases the strength of the glass under static and dynamic loads. For articles strengthened by surface coatings, the resistance to internal hydrostatic pressure increases by $10 – 20\%$, the resistance to pressure on the body increases by $10 – 30\%$, and the resistance to pressure along the height of articles increases by up to 15%. The effectiveness of strengthening coatings increases as the size of the articles decreases.

The protective-strengthening effect is intensified when combined coatings are deposited: on the hot conveyor of the process line articles are treated with tin tetrachloride or titanium tetraisopropyllate vapor, while at the "cold" end of the annealing furnace organic coatings, for example, sintanol, metaupon, preparations based on epoxy resins, and so forth, are deposited on them. These coatings prevent damage to the surface of the articles when they rub against one another. Combined coatings greatly reduce breakage during shipment and on washing-dispensing lines in food plants. Such surface treatment of articles increases the strength and serviceability of articles by $15 – 30\%$.

The characteristics of inorganic and organic coatings deposited on glassware are presented in Table 2.

Evaluation of glass container strength. The strength of glass bottles is evaluated by the internal hydrostatic pressure method. Bottles to be used for champagne, beer, and carbonated beverages must be especially strong; they are subjected to high internal pressure for a comparatively long time. The shape of bottles with transitions from the bottom to the vertical walls, the complex shape of the crown in the manufacturing technology, including the contacts between the glass mass and metal surfaces, rapid cooling, quite high deforming forces acting on the high-viscosity glass mass, and so forth all create the conditions for various defects to appear, first and foremost, very dangerous surface defects. Consequently, for example, the strength of champagne bottles (resistance to internal hydrostatic pressure) is comparatively low and is characterized by a large variance of the strength indicators. In one average sample from a batch, the strength of the bottles can fluctuate from 1.4 to 4.5 MPa. At the same time, these standards give a minimum guaranteed strength for champagne bottles ($1.4 – 1.7$ MPa depending on the holding times). The effect of different factors on the strength of bottles is analyzed statistically.

Figure 3 shows curves of the differential and integral strength distribution functions for three types of champagne

bottles [19]. The most likely strength of the initial of bottles is 2.4 MPa and the minimum guaranteed strength is 1.4 MPa. The distribution of particular values of the strength is shifted leftward. For champagne bottles with the smoothest body-bottom transition the most likely strength is 2.6 MPa and the minimum guaranteed strength is 2.0 MPa. The strength is increased primarily by raising the bottom limit of the strength values. Eliminating low-strength samples, for example, by lowering the local stress concentration at the transitions between the bottom and body surfaces, gives the best structural design for the bottom part of the bottle. Bottles with the best structural design at the bottom were treated with tin tetrachloride vapor on the hot conveyor. The most likely bottom strength increases to 3 MPa and the minimum guaranteed strength increases to 2.4 MPa. A strengthened microlayer is produced on the surface of such bottles, the tin oxide film partially blocks the surface defects, and the strength of the bottles increases. Analysis of the test results makes it possible to determine the probability of bottles breaking under a load which can arise under operating conditions (according to the integral distribution function curves). The main strength parameters of the bottles tested ($1 - 3$) are presented in Table 3. For example, 50% of the bottles (1), 25% of the bottles (2) and no bottles (3) will break under pressure 2.4 MPa.

It is evident from the data in Table 3 that when the average strength increases, the minimum guaranteed values and strength also increase and the standard deviation and variance decrease.

A statistical evaluation of the effect of the temperature of the molds on the impact strength of glass containers was made in [20]. The optimum temperature range for the molds was determined to be $480 - 550°C$. At the same time, the large variance of the impact strength in this range shows that the surface and volume strength factors for glass articles are characterized by a wide collection of defects with different degrees of danger (micro-openings, nonuniformity of the glass distribution, and so forth).

Chemical Stability and Corrosion of Glass. The glass composition and chemical stability indicators (water repellency) of the glass containerware that is manufactured meet the operative norms. Nonetheless, there have been cases where the food products stored in glass containers
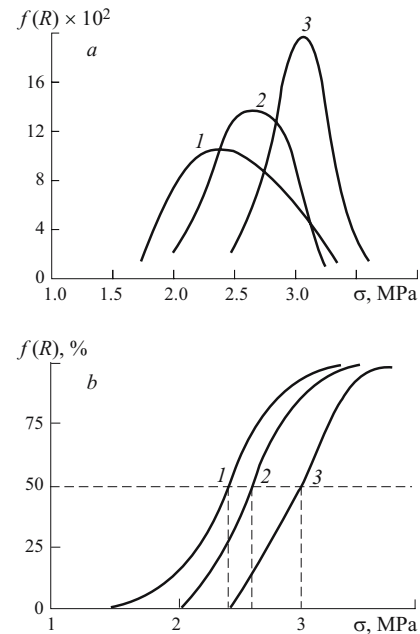

Fig. 3. Curves of the differential (*a*) and integral (*b*) strength distribution functions for champagne bottles: *1*) initial bottles; *2*) bottles with smoother body-bottom transition; *3*) bottles with improved structural design of the bottom part.

made from such glass have spoiled (clouding, settling of sediments, and so forth). This is most characteristic for bottles containing alcohol, especially vodka.

Food products spoil primarily because the state of the contact surface is unsatisfactory, which is due to the storage time and conditions for glass containers which are empty as well as those which contain food products. When empty glass containers are stored for a long period of time, the moisture in the atmosphere engenders chemical corrosion of the inner surface of the glass, which subsequently has a negative effect on the food products. For example, when vodka is dispensed and then stored, a cold precipitate of low-solubility salts of silicic acid can appear in the bottles [21]; this is due to the development of corrosion of the glass and formation of silicic acid gel on the inner surface of the bottle. This is a quite prolonged process, which can be discovered with the aid of an indicator — methylene blue. On contact of the indicator solution with silicic acid gel the positive pigment

TABLE 2.

Characteristic	Coating	
	inorganic (metal oxides)	organic
Water repellency	Average	High
Preservation	High (strength, microhardness, and durability increase)	Low (coatings unstable with respect to abrasion)
Protective effect	Low (thickness up to 1 μm)	High (thickness 50 – 100 μm)

TABLE 3.

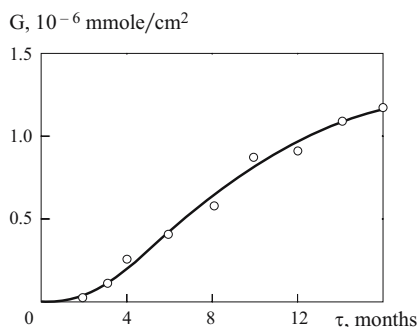| Strength parameters	Values of the parameters for bottles		
	1	2	3
Average strength, MPa	2.52	2.67	3.04
Minimum guaranteed strength, MPa	1.4	2.0	2.4
Standard deviation, MPa	± 0.36	± 0.29	± 0.28
Variance, %	14.2	11.0	9.3

G, 10^{-6} mmole/cm^2

Fig. 4. Kinetics of adsorption G of an indicator on the inner surface of bottles stored on an open site.

ion is adsorbed on the surface of the gel; if gel is present, the inner surface of the bottle acquires a blue color.

The kinetics of pigment adsorption on the inner surface of bottles is presented in Fig. 4. The character of the kinetic curve of pigment adsorption shows that the glass surface corrodes slowly at first. Then the corrosion accelerates and once again slows down as adsorption equilibrium is approached. Comparing the kinetics of pigment adsorption with the character of the surface color, it can be concluded that the process resulting in the destruction of the glass develops nonuniformly, which is due to the facts that the surface layer is chemically nonuniform and the formation rate of silicic acid gel is different on different sections of the surface. This also indicates that the kinetics of the chemical processes resulting in the interaction and appearance of silicic acid gel on the inner surface of bottles can be examined from the standpoint of nucleation [22].

When vodka and alcohol solutions were stored in bottles whose inner surface was corroded, scaly and needle-shaped formations (crystal hydrates of silicic acids) appeared after 1 – 2 months, after which amorphous gel-like precipitates appeared. The appearance of the latter could be due to the formation and polymerization of silicic acids.

On the basis of these investigations and the analysis of practical data, bottle manufacturers and users should focus attention on the following production-technological factors:

glass compositions with adequate chemical resistance should be used; to improve the chemical resistance of the glass, the content of Na_2O should be decreased within certain limits, the amount of CaO should be increased while decreasing the MgO content, the "two alkali effect" should be used, introducing a small quantity of K_2O; this should also improve the glassmaking and production characteristics of the glasses;

the storage times of bottles in packages on open sites should be reduced to a minimum in order to avoid accelerating the corrosion of their inner surface; poor airflow results in high moisture content inside bottles, and the destruction of the surface layer accelerates;

storing bottles on open sites for more than two months is not recommended;

purified air, preferably with controllable purification parameters, such as the content of moisture, oil, and other contaminants, should be used for blowing glass.

Spectral Characteristics of Glass. The spectral characteristics of container glass comprise one of the serviceability factors of glass containerware. For a high-quality colorless containers, it is important to have the highest possible transmission (or lowest possible of absorption) of light incident on the glass. Here, using initial materials of the highest purity (with respect to the content of iron oxides), especially sand, plays the main role. For high-quality colorless glass, the content of iron oxides introduced by the initial materials should not exceed 0.03 – 0.04%. In this case, a weak color tone is easily eliminated by introducing chemical and physical bleaching agents.

Containers made of colored glass are used because of the necessity to protect their contents from the short-wavelength part of the spectrum. However, the protective effect of different colored glasses is not the same. It is preferable to have glass with the highest photoprotective characteristics. At the same time, for high-capacity mechanized production of glass containers it is necessary to use glass which is transparent to thermal (infrared) radiation.

Effect of light on food products. Ultraviolet radiation with wavelengths up to 300 nm and visible radiation up to 500 nm have the largest effect on the state of preservation of food products. Light affects milk, vegetable oils, juices, beer, some types of wine, and other products. For example, sulfur compounds form in beer exposed to light (wavelength 420 – 500 nm) and a "light" aftertaste appears. Milk stored in colorless bottles in daylight rapidly loses vitamin C. Light has a negative effect on vitamins A, B_2, and others. Vegetable oils age and spoil when exposed to light (wavelength 430 – 460 nm).

Ordinarily, commercial colored container glass does not transmit radiation with wavelengths shorter than 300 nm. This is because iron oxides are present in the glass. At the same time, radiation with wavelengths longer than 500 nm does not harm food products.

Diathermancy of colored glasses. During glass making, the diathermancy and, especially, its fluctuations have a large effect on the heating of the glass mass throughout its depth, the formation of glass mass flows, and the thickness of the stationary layer at the bottom. Fluctuations of the diathermancy change the thickness of the bottom layer, where because of gravitational and thermal diffusion phenomena the chemical composition (the content of the components, including the colorants) is different from that of the main layer. As diathermancy of the glass mass increases, this layer is more intensively heated, and it becomes possible for the less heated and nonuniform portions of the glass mass to be drawn into the production flow. All this lowers the overall thermal and chemical uniformity of the glass. As a result, defects in the form of a nonuniform glass distribution and micro-openings, which sharply lower the mechanical strength and heat resistance of a glass container, appear. These defects

are due to the character of the solidification of the glass mass on cooling [23].

Colored glass has a lower diathermancy than colorless glass and are characterized by nonuniform solidification on cooling: they cool more rapidly from the surface and less rapidly in the interior layers. As a result, conditions are created for a nonuniform glass distribution in the walls of the articles formed and the appearance of surface openings.

Evaluation of the photoprotective properties and diathermancy of container glass. On the basis of the data presented above, the results of spectral photometric measurements of radiation transmission in the range $300 - 500$ nm can be used to assess the protective properties of colored container glass [24]. The long wavelength part of the spectrophotometric curve ($1000 - 1100$ nm) must be taken into account when evaluating the diathermancy of glass. In this connection, the ideal glass for colored containers would be glass with a steep absorption boundary near 500 nm and good transmission in the infrared region of the spectrum.

The photoprotective properties of colored container glass can be determined from the ratio of the incident and transmitted radiation in the range $300 - 500$ nm. This is expressed on the plot of the spectral transmission by the ratio of the area of the rectangle with base $300 - 500$ nm and sides corresponding to 100% transmission to the area of the figure with the same base but a limited section of the transmission curve (Fig. 5). The photoprotective index obtained shows the decrease in the fraction of entering light flux as result of the protective effect of the glass. The index increases as the photoprotective properties improve.

The diathermancy index can be determined by decreasing by a factor of 10 the transmission of radiation with wavelength 1100 nm (see Fig. 5). Analysis of the experimental and production data confirms the possibility of making such an estimate of the diathermancy of glass. The idea here is to decrease the transmission in the near-IR region of the spectrum depending on the presence of coloring oxides. The chosen wavelength is most sensitive to the concentration and temperature changes of the transmission of coloring oxides in the glass (mainly FeO and Cr_2O_3); FeO has a strong absorption band in this region of the spectrum while Cr_2O_3 does not. In addition, transmission (absorption) changes as a function of temperature are observed in this region.

The spectral transmission curves presented in Fig. 5 characterize the extreme values, while all other glasses show intermediate transmission values. On the basis of the proposed estimate, colored container glass can be arranged as follows (in decreasing order):

according to photoprotective characteristics: brown (amber), and emerald-green (Cr_2O_3 and $Cr_2O_3 + Fe_2O_3$), dark green ($Fe_2O_3 + FeO$);

according to diathermancy: emerald-green (Cr_2O_3 and $Cr_2O_3 + Fe_2O_3$), brown (amber), dark green ($Fe_2O_3 + FeO$).

High-quality articles made of colorless and colored glass can be produced with rejects reduced to a minimum only by strictly adhering to the technological rules at all stages of
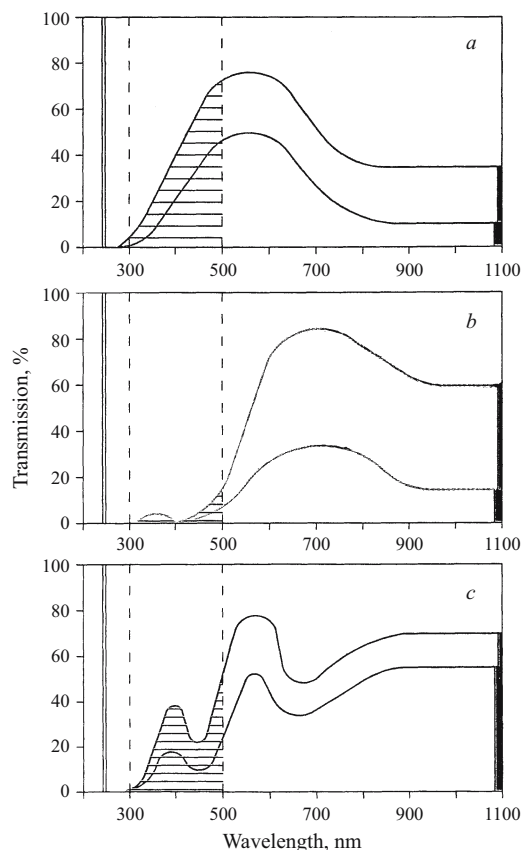

Fig. 5. Evaluation of the photoprotective power and diathermancy of container glass: *a*) dark green glass $[FeO_6]^{3-}$; *b*) amber and brown glass $[FeO_3S]^-$; *c*) emerald-green glass $[CrO_6]^{3-}$ (the formulas in charge of the coloring complexes are indicated).

production starting with the composition of the initial materials. The technological characteristics of glass making and formation (oxidation-reduction potentials of the charge and glass, composition and quality of the cullet, and so on) must also be taken into account.

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